APPLICATIONS OF GROUP THEORY TO THE VIBRATIONS OF METHANE MOLECULES IN THE GASEOUS AND SOLID PHASES

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by

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We present a discussion of the application of group theory to the particular case of solid methane, in all its crystalline phases.

We also employ the quantum mechanical mean approximation to derive the mean square angle of deviation of the methane free molecule. By means of group theory we derive the normal modes, the symmetry coordinates and the nuclear spin functions of methane, which may be found useful for many other purposes in the study of methane. Finally, using these results, we give a discussion of the infrared and Raman spectra, based on group theory again, to explain the observed transitions of the methane molecule in its condensed phases. We conclude that the λ -type transitions are caused by changes in molecular orientation. Phase I is probably disordered, while phase II has structure of symmetry D_{2d} . Phase III (of CD_{4}) is ordered but of lower symmetry and unclear structure.

A possible explanation probably requires an arrangement having more molecules per unit cell than in phases I and II.

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INTRODUCTION

In I929 Clusius⁽¹⁾noted the existence of a γ -type singularity in the spe cific heat of the solid CH₄ at 20.4°K. In I939 an X-ray study carried out by A.Schallamach⁽²⁾revealed a f.c.c structure of the molecular lattice both above and below 20.4°K. This result was also confirmed and extended to all phases of CD₄ in a recent measurement by Greer and Meyer⁽²⁾who working with more recent instruments did not notice the parasitic lines which had been observed by Shallamach in the powder pattern of CH_h.

The different theoretical and experimental studies on methane, which will be reffered to below, have led to the important and final conclu sion, that the observed phase transitions correspond to changes in the orientational structure of solid methane. As the methane structure could not be fully understood from experimental studies only, theoretical predictions have helped provide a basis for the discussion of the experimental results . Among these the molecular field approximation used by James and Keenan⁽⁴⁾ which is fully developed in this work(Ch.II) has proven the most succesful. They discussed the three solid phases of CD_4 , treating the crystal as an f.c.c array of spherical rotators, where molecular and lattice vibrations were neglected. In the interaction potential only octopole-octopole terms between nearest neighbours are retained, lower multipoles, disappearing by symmetry in an undistorted methane tetrahedron.

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On the other hand Nagamiya studied how the energy levels of the free rotator are split by the crystal field due to the neighbouring molecules.

Only little additional insight concerning the arrangement of the me thane tetrahedra can be gained from IR-absorption and Raman scattering, due to the lack of one to one correspondence between observed lines and the symmetry of the unit cell. In addition, it seems questionable whether the instrumental resolution available in these measurements was sufficient. In any case we discuss here the experimental results of Anderson and Savoie on the basis of group theory and we come to the same conclusion as the others by different procedures, concerning the structure of the phases of solid methane.

Recently another method was employed by W.Press⁽⁷⁾ for a better understanding of the orientational structure of methane, that of neutron diffraction. Here again, as all methods have shown, it was found that Phase I is disordered. The structure of phase II was found to agree with that predicted by James and Keenan⁽⁴⁾ It was also found that Phase III seems to arise by small distortions of the orientational structure in phase II.

In general, in discussions of the structures of the three solid phases of CH_4 and CD_4 , everyone agrees, that the carbon atoms occupy f.c.c lattice sites in phases I and II, and that this picture may be taken as a good approximation for phase III.

In our discussion we add the possibility of a probable rearangement of the unit cell in phase III to one having more molecules, as indicated by the experimental results of the infrared spectra of Anderson and Savoie.

Thus the phase changes may readily be understood as transitions

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in the orientational order of the methane tetrahedra.

The above conclusion constitutes the most valid explanation.

CHAPTER I

NORMAL MODES OF VIBRATION OF THE FREE MOLECULE

INTRODUCTION

The determination of the normal modes of a system and their frequency of vibration is very often a tedious process. Group theory can be used to en able some simplification.

The definition of normal coordinates means that the Lagrangian of the system can be expressed in terms of squares of the normal coordinates and their derivatives only.

So the K.E and the P.E are writen in terms of normal coordinates.

$$T = \frac{1}{2} \sum_{i=1}^{3N} \hat{Q}_{i}^{2} \qquad (I)$$

$$V = \frac{1}{2} \sum_{i=1}^{3N} (\omega_{i} \hat{Q}_{i})^{2} \qquad (2)$$

where Q_i are the normal coordinates, forming a coordinate basis where T and V are diagonal in this particular representation.

In case of molecules, N is the no. of atoms (N atomic molecule), 3N is the no. of degrees of freedom, j labels the jth atom executing small oscillations around equilibrium and Q_j is the displacement from equilibrium.

Introducing canonical momentum

$$P_{j} = \frac{\partial T}{\partial \dot{q}_{i}}$$
(1.3)

eqns (I.I) and (I.2) can be used to construct the Quantum mechanical Hamiltonian, which is writen in terms of normal coordinates

$$H = \frac{I}{2} \sum_{j=1}^{3N} (p_j^2 + \omega_j^2 q_j^2)$$

and using $\hat{p}_j = -\frac{\partial H}{\partial Q_j}$ we get eqns of motion :

 $\hat{q}_{j} + \omega_{j}^{2} q_{j} = 0$ (I.4)

having solution

$$Q_{j} \equiv Q_{j}^{0} \cos(\omega_{j}t + \varphi) \qquad (I_{\bullet} 5)$$

where $\omega_j = 2\pi v_j$ is the frequency of the jth normal mode.

If we now take a molecule and perform a symmetry operation on it, then the physical state of the molecule is unaffected by this operation, so that T,V and L are invariant under transformation of the coordinates Corresponding to this operation.

The normal modes of vibration

We shall set up now, the general method which can be used for any molecule which belongs to a symmetry group and then this general method will be applied in the case of the Tetrahedral (T_d) symmetry group which methane (CH_L) belongs to.

Let us consider a system (molecule) consisting of N particles (atoms)at their sites. If energy is imparted to the molecule (shaken), then each atom will execute a complex vibratory motion around its equili brium position, in such a way that the motion of all the atoms is in phase.

A basic requirement is, of course, that the net result of this motion is such that, there is no translation or rotation of the molecule (Naturally, if it happens all the molecules at the same instant of time to move in the same direction, the molecule will translate along this direction, so these modes will be translational.) There are , of course, three translational and three rotational modes. For linear molecules thereare only two rotational degrees of freedom, be cause rotations can only take place around two axes, So for polyatomic molecules or ions remain 3N- 6 vibr. degrees of freedom and for li near molecules or ions 3N - 5 vibr. degrees of freedom.

STEPS

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a.) Establish a set of Cartesian vectors x_i , y_i , z_j on each atom i at its equilibrium position, representing the displacement of the atom from equilibrium.

b.) Determine the dimension of configuration space 3N, where N is the no. of atoms of the molecule and deduce the vibratory degrees of free dom.

c.) Deduce the "symmetry group" of the equil. positions(i.e to accomoda te the molecule to one of the known symmetry groups). Write down the character table of the group.

d.) Deduce from geometrical considerations the characters $\chi(R)$ of the 3N X 3N representation Γ_{3NX3N} . To calculate the characters of Γ_{3NX3N} consider the ff.

i.) Only those nuclei contribute to the characters, which transform into themselves; that is in the 3N X 3N "supermatrix" that corresponds to - Γ_{3NX3N} representation for the whole molecule ,observe that only those atoms contribute to the character of the particular operation R, which do not move when the system is subjected to this certain operation R. In the 3N X 3N supermatrix representing R, all the 3X3 submatrices cor responding to the particles which change position are displaced from the diagonal (so they do not contribute to the character), on the other hand for each undisplaced particle there is a 3X3 matrix whose diagon -al coincides with the diagonal of the 3N X 3N supermatrix.

ii.) A C_n^k operation (rotation) contributes for each undisplaced atom-I+2cos $\frac{20k}{n}$ to the character of the supermatrix

$$\chi(c_n^k) = 1 + 2\cos\frac{2n\kappa}{n}$$
 (1.6)

where k, is the no.of units of rotation.

A S_n^k , improper rotation, contributes for each undisplaced atom;

$$\chi(S_n^k) = -I + 2\cos\frac{2\pi K}{n} \qquad (I.7)$$

A σ operation(reflection on a plane), $\chi(\sigma) = +1$, and Identity al ways $\chi(E) = 3N$. (I.8).

e.) From the characters $\chi(\mathbf{R})$ of the Γ_{3NX3N} representation, subtract the characters $\chi_{\mathbf{T}}(\mathbf{R})$ belonging to translations and $\chi_{\mathbf{R}}(\mathbf{R})$ belonging to rotations, which are known since translations transform like x, y, z, and rotations like $\mathbf{R}_{z}, \mathbf{R}_{y}, \mathbf{R}_{z}$ and exist in the character tables of the group.

So the characters of the representation corresponding to vibrato ry degrees of freedom is;

$$\chi_{\rm V}^{\rm (R)} = \chi_{\rm (R)} - \chi_{\rm T}^{\rm (R)} - \chi_{\rm R}^{\rm (R)}$$
 (1.9)

f.) Decompose the Γ_{3NX3N} acc. to formula:

$$\Gamma_{3NX3N} = \sum_{i=1}^{K} c_i \Gamma_i$$
 (1.10)

where Γ_i are representations of the T_d group and:

$$C_{i} = \frac{4}{h} \left[\sum_{k} N_{k} \chi_{i}(R) \chi(R) \right] \qquad (1.11)$$

where C₁, specifies the independent normal modes.

Application to methane :

Following the previously reffered steps, we define and decompose mo tion along three Cartesian axes x_1, y_1, z_1 , situated at the equilibrium position of every atom. (fig. I). Methane has N=5 atoms, Hydrogen H(A) H(b), H(c), H(d) and Carbon (C), so $3N_{-}$ ¹⁵ degrees of freedom and $3N_{-6-}$ 9vi br.degrees of freedom.

The point group of CH_4 is the full tetrahedral T_d having character table(T.I.I). We deduce the characters of the T_{3NX3N} representation (of the T_{15X15} supermatrix), the characters will be $\chi(E) = 15$, $\chi(C_2) = 1 + 2\cos\frac{2\pi}{2}$ = -1 for each unmoved atom, since in these rotations C_{2x} , C_{2y} , C_{2z} , all atoms move about x, y, z, except the Carbon at the origin of xyz; so only the carbon contributes in the character(the rest are off diagonal).

So $\chi(c_2) = -I$.

Similarly $\chi(C_3) = 0$ for every unmoved atom, so $\chi(C_3) = 0$ for the super matrix.

 $\chi(\sigma) = I$ for each unmoved atom, every diagonal plane contains 2H at oms plus the carbon, i.e three atoms which naturally are unchanged as being on the plane, so for any one of the reflection planes there are three unmoved atoms and so three non zero diagonal elements in the supermatrix, there fore $\chi(\sigma) = 3$.

 $\chi(s_4) = -I$, since only the carbon atom remains unmoved in this operation.

We tabulate the characters of the T_{15X15} representation in table (T.I.2).



The methane molecule with the Cartesian axes at the site of each of the five atoms, indicating the three components of the displacement from equilibrium.

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T.	.I	°I	
	-	-	

T _d (43m)		Е	80 ₃	30 ₂	60 _d	65 ₄	
$x^2 + y^2 + z^2$	AI	I	I	I	I	Ţ	
	A2	I	I	I	I	-1	
$x^2 - y^2$,	Е	2	<u>I</u>	2	0	0	
∕/ʒ(2z ⁻ -x ⁻ -y ⁻) ^R x ^{, R} y ^{, R} z	тI	3	0]	. -]	I	
x,y,z xy,yz,zx	^т 2	3	0	- I	I	-1	

T.I.2

Representation	E	³⁰ 2	80 ₃	60 _d	65 ₄		
r 15 x 15	χ(R)	15	- I	0	3	-I	

Translations transform like x_y, z_y and from (T.I.I), we see that , they transform acc. to T_2 :

So $\chi_{T}(R)$ 3 O -I I -I Rotations transform acc. to $R_{\chi}, R_{\gamma}, R_{\chi}$ and from (T.I.I), we see that, they transform acc.to $T_{I^{\circ}}$

We then tabulate these in (T.I.3), where $\chi_v = \chi_{15\chi_{15}} - (\chi_T + \chi_R)$.

Representation I_{15X15} is decomposed acc. to the formulae(I.IO), (I.II):

Here

$$C_{A_{I}} = \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} = \begin{bmatrix} I \\ I \\ I \\ I \end{bmatrix} = \begin{bmatrix} I \\ I \\ I \end{bmatrix} = \begin{bmatrix} I \\ I \\ I$$

and similarly:

$$C_{A_2} \simeq 0, C_E \simeq C_{T_1} \simeq 1, C_{T_2} \simeq 3$$

So Γ_{15X15} is decomposed as:

$$\mathbf{T}_{\mathbf{15}\mathbf{X}\mathbf{15}} = \mathbf{A}_{\mathbf{I}} + \mathbf{E} + \mathbf{T}_{\mathbf{I}} + \mathbf{3}\mathbf{T}_{\mathbf{2}}$$

and since I_T , I_R , are T_2 , T_1 , respectively, we have finally:

$$\Gamma_{v} = \Gamma_{15X15} = (\Gamma_{T} + \Gamma_{R}) \cong \Lambda_{I} + E + 2\Gamma_{2}$$

These representations correspond to nine normal modes of the metha ne molecule. Any vibrating system that possesses a set of symmetry oper ations, the normal modes of that system "belong to" or "transform according to" one of the irred.representations of the group of those symmetry operations.

If the dimension of the representation is greater than unity, this

	E	8c ₂	30 ₂	6 _{0d}	6.5 ₄	
F 15 x 15	15	0	- I	3	-I	$A_{I} + E + T_{I} + 3T_{2}$
$r_{ m r}$	3	0	-I	I	-I	^T 2
\mathbf{r}_{R}	3	0	-I	-I	I	τ _I
$\Gamma_{T} + \Gamma_{R}$	6	0	-2	0	0	T _I +T ₂
r _v	9	0	I	3	-1	$A_1 + E + 2T_2$
						1

T.I.3

means that there is a set of normal modes , equal in number to the dimen sion of the representation, all of which have the same frequency of vibra tion. They are said to constitute a set of "degenerate normal modes".

The individual normal modes can be thought of as the components of a vector which forms a basis of this irred. representation, that is, the degeneracy of the normal modes equals the dimension of the irred.re presentation to which it belongs.

In methane, we have ; one non degenerate, one two-fold degenerate and two three-fold degenerate normal mode frequencies.

We draw these normal modes: A_I mode simplest : called "totally symmetrical" or "breathing mode" (fig.3). In this all the H atoms have displacements along the directions of the C-H bonds, being equal in magnitude and all directed outwards from the C atom, which itself remains at rest.

Threefold T_2 : To determine the nature of the threefold degen.normal modes, we use the fact that these normal modes form a basis of the degene rate representation T_2 of the point group of the molecule. There are two sets of functions which transform acc. to T_2 : the (x,y,z) and the(xy, yz,zx); so the directions of normal modes will be along x,y,z, in the one set(fig.4), and on the planes(along the diagonals) in the other set. (fig.5). The fact , that we must no have translational motion, allows us to consider the motion of the carbon atom in opposite direction of the motion of the H atoms.

Twofold E :(fig.6) shows how the 2-dim.normal modes move.

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I4



T2(Three dimensional) NORMAL MODES OF THE METHANE MOLECULE







Z

f.3



fig.4







xy

Symmetry coordinates :

Displacement pattern of atoms can be represented in terms of internal coordinates" (such as spacing between atoms, angles between bond directions) or in terms of "external coordinates" (such as Cartesian or Polar).

Introduce "Symmetry coordinates" as linear combination of the inter nal coordinates, which transform irreducibly according to the representations of the symmetry group of the molecule.

$$\mathbf{S}(\mathbf{r}_{g}) = \mathbb{N} \sum_{R} \left(g(R) R \mathbf{s}_{I}^{(g)} \right)$$
(1.12)

where according to the definition $S(T_g)$ is symmetry coordinate transforming acc.to irreducible representation T_g , expressed as linear combination of the internal coordinates RS_I , where S_I is any internal coordinate, R is any symmetry operation of the group RS_I is the internal coordinate that results from applying operation R to S_I , and N is some normalization factor. Remark: As we see RS_I consists of a set of all possible values that an internal coordinate can take, for these values a table will be constructed.

The internal coordinates in general, may differ from the normal co ordinates of the molecule.

In molecules in general we take as internal coordinates, interatomic distances and angles between the atomic bonds, so in our procedure, we use our internal coordinates as a basis for two representations Γ_g ; the Γ_r or $\Gamma(r)$ of distances between the atoms and Γ_g or $\Gamma(e)$ of the angles between the different r_i and r_j 's and form the character table, applying the operations of the group and simply counting the number of unchanged coordinates. In constructing the character table, we have always $\chi^1(E)$ equ al to the no. of symmetry coordinates of type i (e.g: $\Lambda^r(E)$ character of symmetry coordinate of type r). Another fact which arises here, as we shall see is that among the number of irreducible representations we get such ones which do not appear when we calculate the normal modes, as we did before.

Because of this ,we get no. of internal coordinates more than the number of degrees of freedom(in the case of methane we obtain IO int.coor dinates $6\theta_{ij}$, and $4r_i$, that is one more than the 9 degr. of freedom).

This will cause a "redundancy", which is expressed in the presence of the same representation(A_{I} in CH_{4}) in both Γ_{r} , $\Gamma_{\Theta^{\circ}}$

Finally the redundant representation will be excluded.

Symmetry coordinates of the methane molecule:

We choose the internal coordinates to be the distances r_{j} between the atoms C and the H(i)'s and the angles Q_{ij} between the r_{i} and r_{j} 's.

In fig.6 are shown $r_{j} = r_{I}, r_{2}, r_{3}, r_{4}$ and $\Theta_{ij} = \Theta_{I2}, \Theta_{I3}, \Theta_{I4}, \Theta_{23}, \Theta_{24}, \Theta_{34}$ so $\chi^{r}(E) = 4$ and $\chi^{\Theta}(E) = 6$ (Θ_{ij} , is unchanged when r_{i} , and r_{j} are interchan ged, so we do not count distinctly Θ_{ij} and Θ_{ji}).

We form now the character table (T.I.4) for the two representations $\Gamma(r)$ and $\Gamma(\Theta)$; as an illustration we give the derivation of the character for the operation C_3 . Rotating about C_3 axis, that is along some r_i the only one r_i which does not change is the one around which we rotate so $\chi^{\Gamma}(C_3) \equiv I_{\infty}$

We decompose now the representations Γ_r and Γ_0 into the representations of the T_d group using (I.IO),(I.II); so $C_{A_1} = C_{T_2} = I$ and $C_E = C_{A_2} = C_{T_1} = 0$, therefore (I.IO) gives:

$$\mathbf{\Gamma}_{\mathbf{r}} = \mathbf{\Gamma} (\mathbf{r}) = \mathbf{A}_{1} + \mathbf{T}_{2} \qquad (\mathbf{I}_{\cdot} \mathbf{I}_{3})$$

for I (0) representation $C_{A_{I}} = C_{E} = C_{T_{2}} = I$ and $C_{A_{2}} = C_{T_{I}} = 0$; so $\Gamma_{\Theta} = \Gamma(\Theta) = A_{I} + E + T_{2}$ (I.14)

We see immediately that A_{I} exists in both (I.I3) and (I.I4) so it is redundant.We derive the symmetry coordinates now by taking the linear combination of the internal coordinates r_{i} 's and Θ_{ij} 's.

Choose $S_{I} \equiv r_{I}$ internal coordinate; the following table (T.I.5) shows how r_{I} transforms under the different operations of the group ; in this specific case r_{I} goes to itself under E, it goes twice into itself under



fig.6 - The internal coordinates $r_1 = r_1, r_2, r_3, r_4$ and $\theta_{ij} = \theta_{12}, \theta_{13}, \theta_{14}, \theta_{23}, \theta_{24}, \theta_{34}$ of the methane molecule.

T.I.4

Л	d	E	C3	°2	s ₄	۳ _d	
ľŗ	I(r)	4	I	0	0	2	A _I tT ₂
Γ_{Θ}	P(0)	6	0	2	0	2	A _I +E+T ₂

T.I.5

	1	r ^I	I	r.I.5					
R	r _ī	<u>r</u> 2	r3	r ₄	<u>χ(</u> A ¹) <u>)</u> (T ₂)		
E	I	0	0	0	I	3			
8c3	2	2	2	2	I	0			
30 ₂	0	Ï	I	I	I	_			
65 ₄	0	2	2	2	I	-I			
60 _d	3	I	I	I	I	I			
	ļ	r.	Ţ	.I.5a	ł				
R	r _T	r ₂	r _z	r _h	χ(A ₎) <u> </u>	,)	n de la compañía de l	ananda an
E	0	I	0	0	I	- 3	ningi artistandi kilometi		
8C ₃	2	2	2	2	I	0			
30 ₂	I	ο	I	I	I	I			
65 ₄	2	0.	2	2	I	-1			
60 _d	I	3	I	I	I	I			
	 	Rrz	I	.I.5b	•				
R	r _T	r ₂	rz	r ₄) X (A)) (T ₂	<u>,</u>)		996 (1997) - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -
E	0	0	I	0	I	3			
8C ₃	2	2	2	2	I	0			
30 ₂	I	I	0	I	I	₽»Ţ			
65 <u>,</u>	2	2	Ο	2	I	J			
60 ₀	I	I	3	I	I	I			
-									

rotation $\pm \frac{2\pi}{3}$ around itself, it goes twice into r_2 under rotation $\frac{2\pi}{3}$ around r_4 and $-\frac{2\pi}{3}$ around r_3 respectively etc.

We also include in the tables the characters of the representations of the T_d group, which exist in the decomposition of the T_r ; similarly tables are constructed for the rest of the coordinates $S_2 = r_2$, $S_3 = r_3$ etc. The tables for the rest coordinates are constructed using symmetry considerations.

Using (I.I2), (I.I3) and (T.I.5), we get

$$S_{I}(A_{Ir}) = N \sum_{R} \chi_{A_{I}(R)Rr_{I}}$$

$$= N [\chi_{A_{I}}(E)r_{I} + \chi_{A_{I}}(C_{3})^{2r_{I}} + \chi_{A_{I}}(C_{3})^{2r_{2}} + \chi_{A_{I}}(C_{3})^{2r_{3}} + \chi_{A_{I}}(C_{3})^{2r_{4}} + \chi_{A_{I}}(C_{3})^{2r_{2}} + \chi_{A_{I}}(C_{2})r_{4} + \chi_{A_{I}}(S_{4})^{2r_{2}} + \chi_{A_{I}}(S_{4})^{2r_{3}} + \chi_{A_{I}}(S_{4})^{2r_{4}} + \chi_{A_{I}}(S_{4})^{2r_{2}} + \chi_{A_{I}}(S_{4})^{2r_{3}} + \chi_{A_{I}}(S_{4})^{2r_{4}} + \chi_{A_{I}}(S_{4})^{3r_{I}} + \chi_{A_{I}}(S_{4})^{2r_{2}} + \chi_{A_{I}}(S_{4})^{2r_{4}} + \chi_{A_{I}}(S_{4})^{3r_{I}} + \chi_{A_{I}}(S_{4})^{2r_{2}} + \chi_{A_{I}}(S_{4})^{2r_{4}} + \chi_{A_{I}}(S_{I})^{2r_{2}} + \chi_{A_{I}}(S_{I})^{2r_{2}} + \chi_{A_{I}}(S_{I})^{2r_{4}} + \chi_{A_{I}}(S_{I})^{$$

and similarly

$$s_{I}(T_{2r}) = \frac{1}{2\sqrt{3}} (3r_{I} - r_{2} - r_{3} - r_{4})$$

Since T_2 is a three dimensional representation there are two other partners $S_2(T_{2r})$ and $S_3(T_{2r})$ which have the same form as S_I and are calcu lated using symmetry considerations (simply we interchange cyclicly the internal coordinates); these partners are tabulated in table 7 (T.I.7).

	Ke ^{IS}		,	L.T.P						
R	Θ _{I2}	θ _{I3}	Θ _{I4}	⁰ 23	⁰ 24	Θ ₃₄	<u>)</u> χ(₄	ι) χ (Е) <u>(</u> Т ₂)	
E	I	0.	ô	0	0	0	I.	2	3	
80 ₃	0	2	2	2	2	0	I	- I	0	
30 ₂	I	0	0	0	0	2	I	2	- I	
65 ₄	0	I	I	I	I	2	I	0		
6 _{°d}	2	I	I	I	I	0	I	0	I	

For the Γ_{Θ} representation, choose $S_{I} = \Theta_{I2}$ and using the same procedure as for (T.I.5) we construct (T.I.6).

Using then (I.I2), (I.I4) and (T.I.6) we get

$$s(A_{10}) = N \sum_{R} \chi_{A_{1}}(R) R \theta_{12} = \frac{4}{\sqrt{6}} (\theta_{12}^{+} \theta_{13}^{+} \theta_{14}^{+} \theta_{23}^{+} \theta_{24}^{+} \theta_{34}^{+})$$

For the two-fold representation we calculate similarly the two partners $S_{I}(E_{\Theta})$ and $S_{2}(E_{\Theta})$, where the second partner is derived using coordinate $S_{2} = \Theta_{I3}$ and constructing table (T.I.6a) simply from(T.I.6) interchanging Θ_{I2}, Θ_{I3} and Θ_{24}, Θ_{34} .

Finally we derive the three partners $S_{I}(T_{2\Theta}), S_{2}(T_{2\Theta})$ and $S_{3}(T_{2\Theta})$ of the three dimensional representation which are tabulated in(T.I.7).

In the Table 7 we have excluded the redundant coordinate $S(A_{I\Theta})$ (we must have one coordinate in the one dim. representation).

The symmetry coordinates are not to be confused with the normal coordinates of the molecule, but they transform according to irred.repre sentations of the group. They also do not diagonalize the secular equation that gives the eigenfrequencies, but if K.E and P.E are expressed in terms of them, the determinant appears in block form, each correspond ing to certain representation of dimension equal to the number of linear independent symmetry coordinates associated with that representation.

The two modes $T_2(r)$ and $T_2(\Theta)$ are actually mixed in the sense that the molecule does not vibrate according to symmetry coordinates cor responding to $T_2(r)$ and $T_2(\Theta)$ but acc. to a motion which is a linear combination of these two. The frequency of vibrations can be found by solving the eigenvalue problem for each block.



SYMMETRY COORDINATES FOR METHANE XY4

$$A_{I}(r) = S(A_{Ir}) = \frac{I}{2} (r_{I} + r_{2} + r_{3} + r_{4})$$

$$T_{2}(r) = S(T_{2r}) = \frac{1}{2\sqrt{3}} (3r_{I} - r_{2} - r_{3} - r_{4})$$

$$\frac{1}{2\sqrt{3}} (3r_{2} - r_{I} - r_{3} - r_{4})$$

$$\frac{1}{2\sqrt{3}} (3r_{3} - r_{I} - r_{2} - r_{4})$$

A(G) redundant

$$E(\theta) = S(E_{\theta}) = \begin{cases} \frac{1}{2\sqrt{3}} (2\theta_{12} - \theta_{13} - \theta_{14} - \theta_{23} - \theta_{24} + 2\theta_{34}) \\ \frac{1}{2\sqrt{3}} (2\theta_{13} - \theta_{12} - \theta_{14} - \theta_{23} - \theta_{34} + 2\theta_{24}) \end{cases}$$
$$T_{2}(\theta) = S(T_{2\theta}) = \begin{cases} \frac{1}{\sqrt{2}} (\theta_{12} - \theta_{34}) \\ \frac{1}{\sqrt{2}} (\theta_{13} - \theta_{24}) \\ \frac{1}{\sqrt{2}} (\theta_{14} - \theta_{23}) \end{cases}$$

CHAPTER II

MOLECULAR FIELD APPROXIMATION METHOD

The purpose of this, is to develop and discuss a method known as "molecular field approximation" or "internal field approximation" which is elegant in describing the rotational states in molecular crystals of linear molecules.

The MFA is appropriate when one wants to find a first approxima tion to a fresh crystal statistical problem such as ours which has not been solved before. To do this, we must know the explicit form of the rotational wave functions of a freely rotating molecule.

The results of this method applied to ortho-hydrogen(J_{\pm} I) by-James & Raich, in Nitrogen by P.Dunmore and methane by Yamamoto.⁽¹¹⁾

Through MFA method we shall try to compute all the thermodynamic cal quantities of the system under consideration.

Before we develop the method, we do the necessary approximations i) Since librational modes are studied, we consider the centers of mass of the molecules fixed at the lattice sites, so there is no translation al motion. ii) We ignore the electrons completely due to the fact that there are in their ground states; actually since at $T \sim 20^{\circ}$ K, $KT \sim 10^{-4}$ x20 $\sim .002$ ev and for Hydrogen the energy which must be given from outside to excite an electron from its ground state (n=1) to (n=2) is 16.33 x x 10^{-19} erg. ~ 10 ev, then we are excused to make this assumption even at room temperature $KT \sim 10^{-4}$ x 300 $\sim .03$ ev.

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Description of the system :

After all assumptions, we finally consider a system of rigid rota tors representing the molecules of any crystal with their centers of mass fixed at the points of a rigid lattice (no vibrations).

To describe the orientation of molecule 1, at site 1, since we are concerned with rotations ; the position of the molecules and their interac tion is going to be given in terms of angular coordinates.

The orientation of the ith molecule is given by its polar angle - $(\theta_i, \varphi_i) \equiv \omega_i$ of the internuclear axis with the polar axis taken to the equilibrium direction $\theta_i \equiv 0$ (fig.7). The interaction consequently of the ith and jth molecules, will be represented by a potential function which will be a function of the angular coordinates of their orientations.

The Hamiltonian therefore of the system will be writen as :

$$H_{s} = \sum_{i=1}^{N} H_{i}(\omega_{i}) + \frac{I N N}{2 \sum_{i=j}^{N} V_{ij}} (\omega_{i}, \omega_{j})$$
(II.I)
$$\frac{I}{2 \sum_{i=j}^{N} V_{ij}} (\omega_{i}, \omega_{j})$$
(II.I)

where $H_{i}(\omega_{i})$ is the rotational K.E operator of the ith molecule, V_{ij} the potential energy of the interaction of the molecules i and j depending on the direction of the intermolecular axis.

We shall employ here a quantum mechanical treatment of the prob lem. Construction of the density matrix : Any quantum mechanical ensemble con

sisting of N systems is represented by a density matrix(or density f^{n} in classical mechanics).

Assume that each molecule i can occur in states $\psi_{m}^{i}(\omega_{i})$ where m = 1,2,3,.. are states of a single molecule which form an orthogonal set of functions with probability of occurence of state m; p_{m}^{i} for the ith mo

lecule.

This probability is independent of p_n^j for $i \neq j$, that is, the probability is independent of the state in which another molecule j may be in the crystal, so the one molecule density matrix is writen by definition:

$$P_{i} = \sum_{m} |m\rangle p_{m}^{i} \langle m| \qquad (II.2)$$

where we sum all over the possible states available to the molecule i and every state multiplied by the probability of its occurence.

Since p_m^i is independent of p_n^j then the total wave f^n of the whole crystal can be writen in product form :

$$\Psi_{\{m\}} = \prod_{i=1}^{N} \Psi_{m_i}$$
 (II.3)

where $\{m\}$ denotes the set of the quantum numbers m_1, m_2, \dots that specifies the ψ 's for individual molecules. By the same argument $\psi_{\{m\}}$ describes the - state of the crystal with probability:

$$P_{m} = \prod_{i=1}^{N} p_{m}^{1}$$
(II.3a)

which is the probability that the crystal is in state V_{im} . The density matrix of the crystal consisting of N molecules will

be:

The assumption of statistical independence (II.3a) allows us to factorize the density matrix of the crystal as a product of individual mo lecule density matrices(II.2):

$$P = \sum_{\mathbf{m}} | \mathbf{m}_{1} \mathbf{m}_{2} \cdots \mathbf{m}_{N} \rangle \prod_{\mathbf{i}} p_{\mathbf{m}_{\mathbf{i}}} \langle \mathbf{m}_{1} \mathbf{m}_{2} \cdots \mathbf{m}_{N} |$$

$$= \prod_{i} \left(\sum_{m_{i}} |m_{i}\rangle p_{m_{i}}^{i} \langle m_{i} | \right)$$
$$= \prod_{i}^{N} \rho_{i} \qquad (II.5)$$

where $\bigcap_{i} = \sum_{m_{i}} |m_{i}\rangle p_{m_{i}} < m_{i}|$ is the one molecule density matrix.

Nean field potential: The total potential at the position of the ithmole cule due to all other molecules, or the potential energy of the ith mole cule is

$$\mathbf{u}^{\mathbf{i}}(\boldsymbol{\omega}_{\mathbf{i}}) = \sum_{\substack{\mathbf{j} = \mathbf{n} \\ \mathbf{j} \neq \mathbf{i}}} \sum_{\mathbf{n}} \langle \boldsymbol{\psi}_{\mathbf{n}}^{\mathbf{j}} | \boldsymbol{\psi}_{\mathbf{i}} \rangle \boldsymbol{P}_{\mathbf{n}}^{\mathbf{j}} \qquad (II.6)$$

Energy calculation : The average energy of the system associated with Ψ_{m} when ith molecule is in state m_i and jth molecule in state m_j whi ch of course are orthogonal states is

$$\langle H \rangle_{m_{i}} = \langle \Psi_{m_{i}}^{i} | \sum_{i} H_{i} | \Psi_{m_{i}}^{i} \rangle + \frac{1}{2} \sum_{ij} \langle \Psi_{m_{i}}^{i} \Psi_{m_{j}}^{j} | V_{ij} | \Psi_{m_{i}}^{i} \Psi_{m_{j}}^{j} \rangle$$

$$= \sum_{i} W_{m_{i}}^{i} + \frac{1}{2} \sum_{ij} W_{m_{i}}^{ij} m_{j} \qquad (II.7)$$

where $\mathbf{w}_{m}^{i} = \langle \boldsymbol{\psi}_{m}^{i} | \boldsymbol{H}_{i} | \boldsymbol{\psi}_{m}^{i} \rangle$ (II.8)

is the rotational energy of the ith molecule in state m, and

$$W_{mn}^{ij} = \langle \psi_{m}^{i} \psi_{n}^{j} | V_{ij} | \psi_{m}^{i} \psi_{n}^{j} \rangle \qquad (II.9)$$

is the interaction potential energy of the ith and jth molecules in sta tes m and n respectively (where we have rejected the subscripts of m_{i} , since II.8 and II.9 hold for any state of the set {m}).

The internal energy of the crystal will be a summation over all the possible states multiplied by the probability of their occurence in

the sum:

$$E = \sum_{im} \langle H \rangle_{imi} P_{imi} P_{imi}$$
$$= \sum_{im} w_m^i P_m^i + \frac{1}{2} \sum_{im} \sum_{im} w_{mn}^{ij} P_m^i P_n^j \qquad (II.IO)$$

Use now the fact that $\langle H \rangle = \sum_{m} W_{m} p_{m} = Tr \rho H$, the proof is as folm

lows:

$$\operatorname{TrpH} = \operatorname{Tr}\left[\left(\sum_{m} |m\rangle P_{m}\langle m|\right)H\right] = \sum_{m} P_{m} \operatorname{Tr} \prod_{m} H \quad \text{where} \quad \{m\}\langle m\} = \prod_{m} P_{m} \operatorname{Tr} \prod_{m} H$$

is the projection operator the square of which is the unity operator and its trace unity, therefore

$$Tr \rho H = \sum_{m} P_{m} Tr \prod_{m}^{2} H = \sum_{m} P_{m} (Tr \prod_{m} H \prod_{m})$$
$$= \sum_{m} P_{m} [T_{r} [m] \langle m|H|m \rangle \langle m|] = \sum_{m} P_{m} \langle m|H|m \rangle = \sum_{m} P_{m} W_{m} Q.E.D$$

Combining (II.10),(II.9) and (II.8) we get

$$\mathbf{E} = \sum_{i} \left(t_{r}^{(i)} P_{i} H_{i} + \frac{1}{2} \sum_{i \neq j} t_{r}^{(i)} t_{r}^{(i)} V_{ij} P_{i} P_{j} \right)$$
(II.II)

which is the total energy of the crystal, where tr⁽¹⁾ is the trace over the Hilbert space of the ith molecule.

The total energy of the ith molecule is:

$$E_{i} = \langle H_{i} \rangle + \sum_{j} tr^{(j)} V_{ij} \rho_{j} \qquad (II.IIa)$$

Thermodynamics : We can now define an operator which instead of being multiplicative is additive, namely ln p. This operator has the advantage of being extensive for a large ensemble(i.e proportional to the no. of constituent systems). For a uniform thermodynamic ensemble, this implies proportionality to the volume.

The average value of $\ln \rho$, $\langle \ln \rho \rangle = tr \rho \ln \rho$ aside from constant it is called the Entropy S of the system : $S = -k tr \rho \ln \rho$ (II.I2), where k is the Boltzman's constant and since $\rho = \prod \rho_i$ then $\ln \rho = \sum_i \ln \rho_i$ (II.I3) and since S is additive $S = -k \sum_i tr^{(i)} \rho_i \ln \rho_i = \sum_i s_i$, where $s_i = -ktr^{(i)} \rho_i \ln \rho_i$.

The most important density matrix in physics is the one describ ing a system in thermal equilibrium with the surroundings at Temperat. T.

The entropy at equilibrium $S \rightarrow S_{max}$ and the free energy $F \rightarrow F_{min}$ so $F_{min} = E - TS_{max}$ at equilibrium in temperature T.

Minimizing the above expression w.r.t $\mathcal{P}_{\mathbf{i}}$ we can find the form of the density matrix which describes the system in equilibrium at temp T.

Solving the variational problem, we get the form of F; to be:

$$\varphi_i = \frac{e^{-kE_i}}{Z_i} \qquad (II_*I4)$$

where $Z_{i} = tr^{(i)}e^{-\ell E_{i}}$, and using (II.IIa) the eqn(II.I4) becomes

$$F_{i} = \frac{e^{-\ell [H_{i} + \sum_{j} tr^{(j)} V_{ij} F_{j}]}}{t_{r}^{(j)} e^{-\ell [H_{i} + \sum_{j} tr^{(j)} V_{ij} F_{j}]}}$$
(II.15)

Equation (II.6) is written $U^{i}(\omega_{i}) = \sum_{j} \langle V_{ij} \rangle$ by definition of the mean value and since $\langle V_{ij} \rangle = tr^{(i)} \beta_{j} V_{ij}$ then:

$$\widetilde{v}^{i}(\omega_{i}) = \sum_{j} tr^{(\dot{j})} \varphi_{j} v_{ij} \qquad (1.16)$$

and by (II.15)

$$P_{j} = \frac{e^{-\ell [\widetilde{H}_{j} + \widetilde{U}_{j}]}}{t_{r}^{(j)} e^{-\ell [\widetilde{H}_{j} + \widetilde{U}_{j}]}} = \frac{e^{-\ell [\widetilde{H}_{j} + \widetilde{U}_{j}]}}{Z_{j}}$$
(II.17)

so (II.I6) becomes

$$\langle U^{i} \rangle = \sum_{j} tr^{(i)} \left(\frac{1}{2} \right) e^{-\ell [\widetilde{H}_{j} + \widetilde{U}_{j}]} \quad (II.I8)$$

and the internal energy (II.II) is written

$$E = \sum_{i} tr^{(i)} H_{i} P_{i} + \frac{1}{2} \sum_{i} tr^{(i)} P_{i} \widetilde{U}_{i}$$
 (II.I9)

in terms of molecular field potential.

Entropy, Free energy: Using eqn (II.I2)

$$s = -\kappa \operatorname{trp} \operatorname{inp} = -\kappa \operatorname{trp} \Sigma [\operatorname{inp}; \operatorname{by} (JI.I3)]$$

$$= -\kappa \operatorname{trp} \Sigma [-BE: -(nZ:]] \quad \text{where} \quad E_{i} = \Sigma \operatorname{e_{im}} \Pi_{im}$$

$$= \kappa \operatorname{btrp} \Sigma E_{i} + \kappa \operatorname{trp} \Sigma [\operatorname{nZ}:]$$

$$= \frac{1}{T} \operatorname{trp} \Sigma \operatorname{e_{im}} \Pi_{im} + \kappa \operatorname{lnZ} \quad \text{since} \quad \operatorname{trp} = 1 \text{ and} \quad Z = \prod Z_{i}$$

$$= \frac{1}{T} \sum_{im} \operatorname{e_{im}} \langle \Pi_{im} \rangle + \kappa \operatorname{lnZ} \quad (II.20)$$

where $\operatorname{tr} \rho n_{in} = \langle n_{in} \rangle$ and $\langle n_{in} \rangle = \frac{I}{e^{-\ell \epsilon_{in}} - I}$ and using $\sum_{i} \epsilon_{in} = \sum_{i} \epsilon_{i}$

 $= \sum_{i} (\widetilde{H}_{i} + \widetilde{U}_{i})$ we get finally:

$$\mathbf{S} = \sum_{\mathbf{i}} \frac{1}{\mathbf{T}} \quad (\widetilde{\mathbf{H}}_{\mathbf{i}} + \widetilde{\mathbf{U}}_{\mathbf{i}}) + k \ln \mathbf{Z} \qquad (II.2I)$$

in terms of molecular field.

Free energy is defined as F = E - TS, so using (II.19)

$$\mathbf{F} = \sum_{i} \operatorname{tr}^{(i)} \operatorname{H}_{i} P_{i} + \frac{1}{2} \sum_{i} \operatorname{tr}^{(i)} P_{i} \widetilde{U}_{i} - \sum_{i} \widetilde{\operatorname{H}}_{i} - \sum_{i} \widetilde{U}_{i} - \kappa T \ln Z$$
$$= -kT \ln Z - \frac{1}{2} \operatorname{tr}^{(i)} P_{i} \widetilde{U}_{i} \qquad (II_{\circ}22)$$

Mean deviation angle: By definition the MDA matrix element is

$$\langle \Theta_{k,m} \rangle \stackrel{(J)}{=} \langle \psi_{km} \stackrel{(J)}{=} | \Theta^2 | \psi_{k,m} \rangle$$
 (II.23)

where k = x, y, z refers to space fixed axes (SFA), m = X, Y, Z refers to molecule fixed axes (MFA), $\Theta_{k,m}$ refers to angle between the components of SFA and MFA, $\psi_{k,m}^{(J)}$ are the explicit rotational wave functions of the freely rotating molecule and $\langle \Theta_{k,m}^2 \rangle$ denotes the mean square deviation of the molecular axis from its equilibrium orientation which has taken to be when the SFA and MFA coincide (fig.8).

Employing cosine functions, using trigonometric expansion, we - get (rejecting higher than 2nd order terms) : $\langle \cos^2\theta \rangle = I - \langle \theta^2 \rangle$ and (II.23) becomes

$$\langle e_{k,m}^2 \rangle \approx I - \langle \psi_{k,m}^{(J)} | \cos^2 \Theta | \psi_{k,m}^{(J)} \rangle$$
 (II.24)

Application to methane (free molecule): Since we know the explicit form of the rotational wave functions of a freely rotating molecule, as has been calculated and tabulated by Yamamoto and Kataoka ,we can calculate the MDA using eqn (II.24).

We write down the explicit rotational wave functions taken from (11) Yamamoto:

$$\Psi_{k,m}^{(J)\pm} = \frac{1}{\sqrt{2}} \left[(2J+I)/8\pi^2 \right]^{\frac{1}{2}} \left\{ \begin{array}{c} D_{-k,m} \pm D_{k,m} \\ D_{-k,m} \pm D_{k,m} \end{array} \right\}$$
(II.25)
$$\Psi_{0,m}^{(J)} = \left[(2J+I)/8\pi^2 \right]^{\frac{1}{2}} D_{0,m}^{(J)} (\alpha, \beta, \gamma)$$
(II.26)

special case when k=0, $D(x, \emptyset, \chi)$ are the rotational matrices, which are functions of the Euler's angles thru which the molecule has been rota ted from its standard orientation.

To calculate the MDA, we can also use the relations given between

the rotational matrix elements and the spherical harmonics, taking the phase convention into account.

Using ROSE (Angular momentum theory) we find the relation of rotational matrix to spherical harmonics, for the special case k 0.

$$D_{O,m}^{(J)}(\alpha, \beta, \gamma) = \left[\frac{4\pi}{2J+I}\right]^{\frac{1}{2}} Y_{Jm}^{*}(\beta, \alpha) \qquad (II.27)$$

For the case k=0, eqn(II.24) becomes

$$\left\langle \Theta_{0,m} \right\rangle = \mathbf{I} - \left\langle \Psi_{0,m}^{(J)} \right| \cos^2 \Theta \left| \Psi_{0,m}^{(J)} \right\rangle \qquad (II.28)$$

where now $\Theta_{O,m}$ refers to the angle between the z and Z axes of the two systems. Substituting (II.26),(II.27) into (II.28) we get

$$\langle \Theta_{0,m}^{2} \rangle^{(J)} = I - \langle Y_{Jm} | \cos^{2} \Theta | Y_{Jm} \rangle$$
 (II.29)

where we integrated over χ which contributes $2 \cap$ to the integral and since (II.27) is independent of χ , we set $\chi=0$ arbitrarily.

For the case k=0, a practical method to verify our results is to sum for a specific J, all over the matrix elements for the 2J+I different values of m, so

$$\sum_{m=-J}^{J} \langle \Psi_{o,m}^{J} | \cos^{2}e | \Psi_{o,m}^{J} \rangle = \int_{0}^{2\pi} d\chi \int_{0}^{\pi} d\varphi \int_{0}^{\pi} \cos^{2}e \sin \theta de \left(\sum_{m=-J}^{J} | \Psi_{o,m}^{J} |^{2} \right)$$

= $\frac{1}{3} (2J+1)$ (II.30)
since $\sum_{m=-J}^{J} | \Psi_{o,m}^{J} |^{2} = \frac{2J+1}{2\pi^{2}}$ and $\sum_{m=-J}^{J} \langle e_{o,m}^{2} \rangle^{J} = \frac{2}{3} (2J+1)$ (II.31)

We calculate now the different MDA for J=0,I,2 .

 $J \equiv 0, m \equiv 0$

$$\langle e_{0,0}^{2} \rangle^{J=0} = I - \langle Y_{00} | \cos^{2} \theta | Y_{00} \rangle = I - 0.333 = 0.667$$

J = I, $m = \pm I$,0

Matrix elements: $\langle Y_{IO} | Cos^2 \Theta | Y_{IO} \rangle = 0.6$

$$\langle \mathbf{Y}_{\mathbf{I},\pm\mathbf{I}} | \cos^2 \Theta | \mathbf{Y}_{\mathbf{I},\pm\mathbf{I}} \rangle = 0.2$$

So $\langle \Theta_{c,c}^{2} \rangle^{j=1} = 0.4$ rad. $\langle \Theta_{c,\pm 1}^{2} \rangle^{j=1} = 0.8$ rad. and $\langle \nabla \rangle = 100^{2} \Theta | Y_{c} \rangle =$

and
$$\sum_{m=-1}^{1} \langle Y_{1m} | \cos^2 \theta | Y_{1m} \rangle = 1$$
, $\sum_{m=-1}^{1} \langle \Theta_{0,m}^2 \rangle^{J=1} = 2$
verifying our results.

J=2, m=12, 1, 0

Matrix elements: $\langle Y_{2,\pm 2} | \cos^2 0 | Y_{2,\pm 2} \rangle = 0.141$ $\langle Y_{2,\pm 1} | \cos^2 0 | Y_{2,\pm 1} \rangle = 0.427$ $\langle Y_{2,0} | \cos^2 0 | Y_{2,0} \rangle = 0.523$

So
$$\langle \Theta_{0,c}^2 \rangle^{3/2} = 0.477 \text{ rad}_{o}$$

 $\langle \Theta_{c,11}^2 \rangle^{3/2} = 0.572 \text{ rad}_{o}$
 $\langle \Theta_{c,12}^2 \rangle^{3/2} = 0.858 \text{ rad}_{o}$
and $\sum_{m=-2}^{2} \langle Y_{2m} | \cos^2 \Theta | Y_{2m} \rangle = 1.66$, $\sum_{m=-2}^{2} \langle \Theta_{0,m}^2 \rangle^{3/2} = 3.333$
verifying our results.





Molecule rotated at angles Θ and ϕ from equilibrium.

Molecule at equilibrium.

a (SFA) L -{m-Fa} - 9 ×

Equilibrium orientation of CH_{μ} molecule, when MFA and SFA axes coincide.





fig. 8

fig.7

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CHAPTER III

NUCLEAR SPIN WAVE FUNCTIONS FOR METHANE

Nuclear spin wave functions $\chi(IM_I)$, where I is the total nuclear spin of the molecule and M_I is the component of the above vector on z' axis of the SFF, these are obtained by Clebsch-Gordon method by decomposing the system into constituents and then coupling the angular momenta of the constitu ent parts.

I, operator, obeys the eigenvalue equations

$$I^{2}|IM_{I}\rangle = I(I+i)|IM_{I}\rangle$$
$$I_{z}|IM_{I}\rangle = M_{I}|IM_{I}\rangle$$

The combined vibrational and nuclear spin functions $\chi(\beta_{5}, IM_{I}) = \chi(\beta_{5}) \chi(IM_{I}),$ where $\chi(\beta_{5})$ is the vibrational part, are obtained taking into consideration how the vibrational modes transform(part I). Here β denotes the set of representations of the methane group, according to which the differ ent vibrational modes $\xi = x, y, z$ transform and we have found them to be $\beta = A_{I} T_{2}, E$ (T.I.3).

To construct the spin wave functions for methane, we separate the system (molecule) into two Hydrogen molecules and then combine the wave fu nctions of these, acc. to rules of addition of angular momenta.

There are three different ways of partitioning the four H atoms into two Hydrogen molecules; that is atoms lying on planes perpedicular to x axis (I,3) and (2,4), on planes perpedicular to y axis (I,4) and (2,3) and perpedicular to z axis (I,2) and (3,4) having wave functions $|I_{I,3} m_{I,3}\rangle$ $|I_{2,4} m_{2,4}\rangle$ and so on.

Since $I_{ij} = I,0$ for the Hydrogen molecules, then the total I satisfying the condition :

$$|I_{1,3} - I_{2,4}| \leq |I_{1,3} + I_{2,4}|$$

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must have values I=2,1,0.

Detailed symmetry arguments show how the vibrational functions and nuclear spin functions must be combined (as it was mentioned before) in order to preserve the overall symmetry of the wave function under the ope rations of the group T_d . The result is:

$$\chi(\mathbf{T}_{2}\mathbf{x}_{s}\mathbf{1}_{s}\mathbf{m}_{I}), \chi(\mathbf{T}_{2}\mathbf{y}_{s}\mathbf{1}\mathbf{m}_{I}), \chi(\mathbf{T}_{2}\mathbf{z}_{s}\mathbf{1}\mathbf{m}_{I})$$

$$\chi(\mathbf{E}\mathbf{1}_{s}\mathbf{6}\mathbf{6}), \chi(\mathbf{E}\mathbf{2}_{s}\mathbf{0}\mathbf{0})$$
and $\chi(\mathbf{A}_{I},\mathbf{2}\mathbf{m}_{I})$

$$(III.I)$$

Denote with a, spin up state and with b, spin down state of the individual atoms, so a_{i} , b_{i} where i = 1, 2, 3, 4 are the up and down spin states of the four H atoms; therefore the states $|I, M_{I}\rangle$ are the following, for I = 2, $|22\rangle$, $|21\rangle$, $|20\rangle$, $|2-1\rangle$, $|2-2\rangle$, for I = 1, $|11\rangle$, $|10\rangle$, $|1-1\rangle$ and for I = 0 the $|00\rangle$.

The state $|22\rangle$ arises when all spins are up, so we choose

$$|22\rangle = \prod_{i=1}^{7} a_i = a_1 a_2 a_3 a_4$$
 (III.2)

Introduce the Operators

$$I_{2} = I_{1} + I_{2} + I_{3} + I_{4}$$
 (III.4)

obeying the known rules

$$I_{\pm}|IM_{I}\rangle = \left[I(I+1) - M_{I}(M_{I}\pm 1)\right]^{\frac{1}{2}} |I, M_{I}\pm 1\rangle \quad (III.4)$$

(III.5)

where $I_i a_i = b_i$ and $I_i b_i = 0$

Starting from $|22\rangle$ we derive all the others, operating on (III.2) with the lowering operator (III.4) and taking into consideration(III.3,5)

 $I_{22} = \left[I(I+1) - M(M-1) \right]^{\frac{1}{2}} |2I\rangle = 2|2I\rangle$ and $|2I\rangle = \frac{1}{2}I_{2}|22\rangle = \frac{1}{2}(I_{1}^{-} + I_{2}^{-} + I_{3}^{-} + I_{4}^{-})(a_{1}a_{2}a_{3}a_{4})$, and using (III.5) we get $|2I\rangle = \frac{1}{2}(b_{1}a_{2}a_{3}a_{4} + a_{1}b_{2}a_{3}a_{4} + a_{1}a_{2}b_{3}a_{4} + a_{1}a_{2}a_{3}b_{4})$ and lowering again we construct the rest four wave functions for I = 2 which are tabulated in table (T.III.I) and are properly normalized.

⁽⁴²⁾We calculate now the functions for I=1, which will be orthogonal to functions $|2M_{\rm I}\rangle$, so it must be $\langle 2I|II\rangle = 0.4$ function orthogonal to $|2I\rangle$ will be one derived simply by inspection, having the same form as $|2I\rangle$ but in which we have interchanged the signs of the terms; thus $|11\rangle = \frac{1}{2}$ ($b_{\rm I}a_2a_3a_4$ - $-a_{\rm I}b_2a_3a_4 + a_{\rm I}a_2b_3a_4 - a_{\rm I}a_2a_3b_4$) and using lowering operators again we obtain the rest two functions, which are tabulated in(T.III.I), where in $|I-I\rangle$ we have changed the signs all over, to bring it to the same form as the $|II\rangle$ (only a, and b, having been interchanged).

Here since T_2 representation is threefold we have three set of functions (T_{2x}, T_{2y}, T_{2z}) , that is, another two set of triplets; these sets can be obtained by using symmetry considerations, interchanging the signs of the terms and finally tabulate in (T.III.I) $(\ln |11\rangle, |1-1\rangle$ we interchange simply the roles of a, and b).

By inspection we see that these are not antisymmetric under an ar bitrary interchange of two nuclei; e.g $1 \leftrightarrow 2$ in the function $\frac{1}{\sqrt{2}} (b_1 a_2 b_3 a_4 - a_1 b_2 a_3 b_4)$ gives $\frac{1}{\sqrt{2}} (a_1 b_2 b_3 a_4 - b_1 a_2 a_3 b_4)$ which is one of the other $|10\rangle$ functions with interchanged sign.

So we see that spin triplets are neither symmetric nor antisymmet ric under interchange of two protons.

We form now the singlet wave functions for I=0, we require two

So:

sets of singlet states for the E representation, $\chi(E_{1}^{1},00)$ and $\chi(E_{2},00)$.

We construct them again by inspection using orthogonality considerations of $|00\rangle$ and $|10\rangle$, $|20\rangle$; we therefore choose $|00\rangle$ to have exactly the same form with the $|20\rangle$ with coefficients which will be calculated, us ing the fact that $|00\rangle$ must be orthogonal to $|10\rangle$ and $|20\rangle$ functions.

So

$$| 00 \rangle = \frac{1}{\sqrt{6}} \left\{ c_{1}(a_{1}a_{2}b_{3}b_{4} + b_{1}b_{2}a_{3}a_{4}) + c_{2}(a_{1}b_{2}a_{3}b_{4} + b_{1}a_{2}b_{3}a_{4}) + c_{3}(a_{1}b_{2}b_{3}a_{4} + b_{1}a_{2}a_{3}b_{4}) + c_{3}(a_{1}b_{2}b_{3}a_{4} + b_{1}a_{2}a_{3}b_{4}) \right\}$$

The conditions $\langle 00|20 \rangle = \langle 00|10 \rangle = 0$ and $\langle 00|00 \rangle = 1$ give us the two singlet eigenfunctions which are found together with the others in (T.III.I) These two singlet functions are mutually orthogonal.

T.III.I

VIBRATIONAL_NUCLEAR SPIN WAVE FUNCTIONS FOR THE METHANE MOLECULE

I	M _T	в	ç	X (65, IMI)
2	2	AT		arazaza
	1	-		$\frac{1}{2} \left[b_{1}a_{2}a_{3}a_{4} + a_{1}b_{2}a_{3}a_{4} + a_{1}a_{2}b_{3}a_{4} + a_{1}a_{2}a_{3}b_{4} \right]$
	<u>o</u>			$\frac{1}{\sqrt{6}} \left[b_{1} b_{2} a_{3} a_{4} + b_{1} a_{2} b_{3} a_{4} + b_{1} a_{2} a_{3} b_{4} + a_{1} b_{2} b_{3} a_{4} + a_{1} b_{2} a_{3} b_{4} + a_{1} a_{2} b_{3} b_{4} \right]$
	-1			$\frac{1}{2} \left[{}^{b}{}_{1}{}^{b}{}_{2}{}^{b}{}_{3}{}^{a}{}_{4} + {}^{b}{}_{1}{}^{b}{}_{2}{}^{a}{}_{3}{}^{b}{}_{4} + {}^{b}{}_{1}{}^{a}{}_{2}{}^{b}{}_{3}{}^{b}{}_{4} + {}^{a}{}_{1}{}^{b}{}_{2}{}^{b}{}_{3}{}^{b}{}_{4} \right]$
	-2			^b 1 ^b 2 ^b 3 ^b 4
1	1	T2	x	$\frac{1}{2} \left[(b_{1}a_{2}a_{3}a_{4} + a_{1}a_{2}b_{3}a_{4}) - (a_{1}b_{2}a_{3}a_{4} + a_{1}a_{2}a_{3}b_{4}) \right]$
	0			$\frac{1}{\sqrt{2}}(b_{1}a_{2}b_{3}a_{4}-a_{1}b_{2}a_{3}b_{4})$
	-1			$\frac{1}{2} \left[(a_1 b_2 b_3 b_4 + b_1 b_2 a_3 b_4) - (b_1 a_2 b_3 b_4 + b_1 b_2 b_3 a_4) \right]$
1	1	^т 2	у	$\frac{1}{2} \left[(b_{1}a_{2}a_{3}a_{4}+a_{1}b_{2}a_{3}a_{4}) - (a_{1}a_{2}b_{3}a_{4}+a_{1}a_{2}a_{3}b_{4}) \right]$
-	0			$\frac{1}{\sqrt{2}}(b_1b_2a_3a_4 a_1a_2b_3b_4)$
	-1			$\frac{1}{2} \left[(a_1 b_2 b_3 b_4 + b_1 a_2 b_3 b_4) - (b_1 b_2 a_3 b_4 + b_1 b_2 b_3 a_4) \right]$
1	1	^т 2	z	$\frac{1}{2} \left[(b_1 a_2 a_3 a_4 + a_1 a_2 a_3 b_4) - (a_1 b_2 a_3 a_4 + a_1 a_2 b_3 a_4) \right]$
	0			$\frac{1}{\sqrt{2}}(b_1a_2a_3b_4-a_1b_2b_3a_4)$
	-1			$\frac{1}{2} \left[(a_{1}b_{2}b_{3}b_{4}+b_{1}b_{2}b_{3}a_{4}) - (b_{1}a_{2}b_{3}b_{4}+b_{1}b_{2}a_{3}b_{4}) \right]$
0	0	Е	1	$\frac{1}{2} \left[(a_{T}a_{2}b_{z}b_{z}+b_{T}b_{2}a_{z}a_{z}) - (a_{T}b_{2}a_{z}b_{z}+b_{T}a_{2}b_{z}a_{z}) \right]$
			2	$\frac{1}{\sqrt{2}} \left[(a_1 b_2 b_3 a_4 + b_1 a_2 a_3 b_4) - \frac{1}{2} (a_1 a_2 b_3 b_4 + b_1 b_2 a_3 a_4) - \frac{1}{2} (a_1 b_2 a_3 b_4 + b_1 a_2 b_3 a_4) - \frac{1}{2} (a_1 b_2 a_3 a_4) - \frac{1}{2} (a_1 b_2 a_4) - \frac{1}{2} (a_1 b_2 a_4) $
4			l	

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CHAPTER IV

INFRA RED AND RAMAN SPECTRA AND STRUCTURES OF CRYSTALLINE

PHASES OF METHANE

INTRODUCTION

Crystalline methane is known to have two phase changes at 20.4 $^{\circ}$ K passing from phase I to phase II, and at 8 $^{\circ}$ K passing to phase III for CH₄; the same happens for CD₄ at 27.1 $^{\circ}$ K and 22.2 $^{\circ}$ K respectively.

Specific-heat studies show these to be λ -type transitions and an explanation is that they result from changes in molecular orientation.

This conclusion is also supported by detailed studies of the Infra red and Raman spectra.

It is these latter studies which we shall discuss in the present chapter.

Spectra from crystalline phases of methane:

It is known that an EM wave(radiation) falling on a molecule or solid can induce transitions from one stationary state to another thru coupling with either the dipole moment μ (IR transition), or the polarizabili ty α (Raman induced transition) components. These effects are used to in vestigate the vibrational energy levels of a molecule or solid and tell its structure.

The selection rules impose the condition that a transition between energy levels (i.e transition from one normal mode to another) is possible if the matrix elements $\langle m|p|n \rangle$ differ from zero, where p = x, y, z, $x^2, y^2, z^2, xy, yz, zx$ etc is an operator corresponding to the physical influence causing the transition from one state ψ_m to another ψ_n depending upon the case.

These integrals are different from zero if comparing the direct products of ψ_n and ψ_m with the symmetry species of p,have

$$\Gamma_p \subset \Gamma_{\psi_m} \times \Gamma_{\psi_m}$$

Transition $\psi_n \longrightarrow \psi_m$, where n and m represent a set of quantum numbers de scribing each normal mode, is allowed if $\langle n | \mu | m \rangle \neq 0$, i.e $\Gamma_A \subset \Gamma_{\mu} \times \Gamma_{\mu} \times \Gamma_{\mu} \times \Gamma_{\mu}$ for infra red and $\langle n | \alpha | m \rangle \neq 0$, i.e $\Gamma_A \subset \Gamma_{\mu} \times \Gamma_{\lambda} \subset \Gamma_{\mu} \times \Gamma_{\mu} \times \Gamma_{\mu}$ for Raman induced transitions, where ∞ is the polarizability and μ the dipole moment.

All these selection rules are only valid for a molecule in field free space, that is, one in which no external EM forces are acting ex cept the interaction with the light beam. The effects of the external for ces are even noticeable in the gas phase when the pressure is increased and (3) normally forbidden transitions become IR active.

We have also great differencies between gas, solid and liquid spec tra noticed by Anderson and Savoie. The frequencies of vibration are also very dependent upon the solvent medium.⁽⁴⁾

The normal modes of tetrahedral XY_4 , which were calculated in I.transform as the following representations of T_4 :



where the transformation properties of the components of the polarizability and of the dipole moment are given.

In CH₄ and CD₄ a transition from ground level to level with Q_I singly excited yields: $A_I \propto (T_2)_{\mu} \propto A_I = (T_2)_{\mu}$ which is not IR active as not - containing the A_I , but it is Raman active ($A_I \propto (A_I) \propto A_I = (A_I)$).

By similar calculations transitions from ground level to levels of the type (Q_2, Q_3) are not expected to be IR active, while transitions to - (Q_4, Q_5, Q_6) and (Q_7, Q_8, Q_9) will be IR active. Likewise it can be shown that all transitions from the ground state are expected to be Raman active.

Anderson and Savoie measured the frequencies of the transitions for CH_4 and CD_4 molecules in the crystal which are tabulated in Tables I,II of the paper.⁽⁶⁾ The results are in complete agreement with the predictions based on group theory.

The fact, as well as the absence of IR spectral activity in the V_i and V_2 regions, suggest that the symmetry of CH₄ and CD₄ molecules in the cry stal is substantially tetrahedral. As has been seen, the vibrational spectr um of the free molecule in the gaseous state depends essentially on the sym metry properties of the free molecule. In the condensed state, that is in the crystal, similar but not identical criteria apply.

The arrangement of the molecules in the crystal lattice is given by certain "space symmetry groups" together with the knowledge of how many mole cules occur in the unit cell, characteristics determining the nature of the vibrational spectra of crystals; such a table is given by Savitsky and Horn ig for methane (table II) , based on the X-ray studies on crystalline methane done by A.Shallamach⁽²⁾. These show the carbon lattice to be essentially face centered cubic above and below the critical point 20.4° K.

The necessity now to choose out of the possible space groups for the structure of phase II the ones which put the carbon atoms on face centered positions (allowing three infrared active components for V_{\downarrow}),led Savitsky and Hornig to hexagonal and tetragonal structures with two or four molecules per unit cell in which the carbon atoms lie on sites whose symmetries are subgroups of T_d and fit both their infrared data and the packing requiremen ts;but is found that groups D_{2d}^2 and D_{2d}^3 (from tableII) with two molecules per unit cell on sites of D_2 and C_{2v} symmetry respectively, are most favor -able.

However, the group C_{2v} is rejected since it predicts infrared activity for V_1 and V_2 and these were not observed even in very thin films.⁽⁶⁾

Hence the space groups D_{2d}^2 and D_{2d}^3 represent the best packing and therefore the crystal in phase II has most probably this structure.

In addition it is also consistent with the Raman results of Ander-(6) son and Savoie.

For the problem of phase I, the fact that the position of the peaks

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does not change, as Savitsky and Hornig have noticed , on warming, but the bands broaden significantly (width at 32°K of CH₄ is 9.Icm^{-I} while at 22° is only 5cm^{-I}) supports the evidence for disorder; since the structure is disordered it cannot characterized by a space group (except in an average sense) as phase II.

In phase III we notice that more peaks exist in the absorption spec tra, which means we have further splitting of some lines and consequently a space group of lower symmetry, but this is not exactly the case.

On the one hand V_3 is not further split, while V_4 in the IR spectrum is split into seven components.

Lowering the symmetry from T_d to D_{2d} splits the triply degenerate V_4 mode into a singly degenerate (type B_2) and a doubly degenerate (type E)mode. Furthermore if the symmetry changes to D_2 , this mode splits into three singly degenerate modes (types B_1, B_2, B_3).

In either case table II⁽⁵⁾ shows that there are 2 molecules per unit cell, so that the maximum number of lines that can occur, taking into account the Davydov splitting, is 4 or 6 respectively. So a possible explanation is to require more molecules per primitive cell, but in anyway the situation regarding phase III is unclear, since it is not even known whether the face centered structure is retained in this phase.

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